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(54) Title: METHOD OF CLEANING ARTICLES USING SUPER-CRITICAL GASES**(57) Abstract**

In the fabrication of a variety of articles, organic contaminants become affixed to the surfaces of these articles and must subsequently be removed. The disclosed method is effective for the removal of organic contaminants from a variety of articles, and is efficient to enable the rapid removal of such contaminants without damage to the article. The method has special utility in the cleaning of components used in aerospace applications. In the disclosed method, a structural component bearing the contaminant is contacted in a pressure vessel with a gas under super-critical conditions of temperature and pressure whereby the contaminant is absorbed by the gas. The gas, having the contaminant absorbed therein, is then purged from the vessel to obtain the cleaned component.

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METHOD OF CLEANING ARTICLES
USING SUPER-CRITICAL GASES

BACKGROUND OF THE INVENTION

1 1. Field of the Invention

This invention relates in general to a method of removing contaminants from articles and, in particular, to a simple, rapid and effective method of removing from the surface and interstices of a solid article a variety of contaminants with which the article may possibly have come in contact during its manufacture. More specifically, the present invention relates to a method of removing organic contaminants from such articles using gases in the super-critical state.

10 2. Description of the Prior Art

Components and materials used in the manufacture of instruments and materials used in the manufacture of instruments for aerospace applications must be free from contaminants. The presence of trace amounts of contaminants in components of precision instruments used in space vehicles which ordinarily do not interfere with the operation of these devices on earth, manifest themselves under the conditions of outer space and interfere with the accurate, normal operation of these sensitive devices. Thus, it is critical that the components be free of any and all contaminants, particularly organic contaminants. The contamination



1 of the component may consist of saponifiable materials such as oils as well as non-saponifiable materials such as resins. Components formed from metal or synthetic plastic materials may contain gaseous or vaporizable
5 contaminant residues from the manufacture and processing of the metal such as uncured prepolymers, release agents and unreacted monomers used in the processing of these materials.

To effect the required level of cleaning of the
10 materials used in the manufacture of components which meet government standards for cleanliness, the art has developed cleaning processes for these materials utilizing high vacuum, e.g., 10^{-5} torr (millimeters of mercury or mmHg) and elevated temperatures up to 250°C to remove
15 absorbed and adsorbed organic contaminants from the materials. This cleaning technique, referred to in the art as "thermal vacuum cleaning", is not completely satisfactory in that the cleaning process must be carried out in an expensive and complex high vacuum
20 system which normally requires about fifteen hours to obtain the desired contaminant free surface.

An alternative to thermal vacuum cleaning, used by the prior art to effect cleaning of metal components, is solvent extraction. The solvent extraction cleaning
25 process, in addition to requiring protracted treatment times, has the drawback that when cleaning porous materials, trace amount of the solvent used for cleaning, e.g., chlorinated hydrocarbons, may be adsorbed on the part being cleaned thereby, contributing to the contamination problem.



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SUMMARY OF THE INVENTION

In accordance with the present invention, the rapid removal of organic-based contaminants from articles, both porous and non-porous, without damage or contamination to the article is effected by contacting the article bearing the contaminant in a pressure vessel with a gas under super-critical conditions of temperature and pressure, whereby the contaminant on the surface and/or in the interstices of the article is absorbed by the gas and, thereafter, purging the gas from the pressure vessel to obtain the article having the contaminant removed therefrom. By surfaces is meant not only exterior surfaces but also interior surfaces which communicate therewith.

15

By the practice of the present invention, organic contaminants are removed from articles in one hour or less to achieve a substantially contaminant-free article as compared to thermal vacuum cleaning processes which require fifteen hours or more to achieve an equivalent level of cleanliness and several days of treatment by solvent extraction.

20

As will hereinafter be further demonstrated, by following the practice of the present invention, twice as much volatile contaminant was removed to temperatures near ambient from difficult-to-clean silicone rubber parts in one-fiftieth the time when compared to cleaning equivalent rubber parts using thermal vacuum cleaning.

30

It is known that when the temperature of a gas is above a certain temperature, known as the critical temperature, it is not possible to liquefy the gas by application of pressure alone. It is necessary to reduce the temperature below the critical temperature in order to be able to liquefy the gas. At the critical temperature, as the gas is subjected to increasingly

DETAILED DESCRIPTION OF THE INVENTION

35



1 higher pressure, e.g., on the order of several thousand
pounds per square inch (psi) (one psi equals 51.71493 mm
of mercury), the density of the gas approaches that of
a liquid and the gas acts as a solvent for a variety of
5 different types of organic and organo-metallic materials,
including aliphatic and aromatic hydrocarbon organo-
metallics such as metal alkyls and alcoholates, silicones
and boroalkyls and organic esters or inorganic acids
such as sulfuric and phosphoric acid. The critical
10 temperatures and pressures for a variety of gases at
which they exist in the super-critical condition may be
found in U.S. Patent No. 4,124,528, the teachings of
which are hereby incorporated by reference.

15 In the practice of the present invention, the
article of manufacture to be cleaned is placed in a
suitable vessel such as a pressure chamber or autoclave
and the gas which is to effect the cleaning of the
article surface is admitted to the vessel in a super-
critical condition.

20 Cleaning of the article is accomplished in the
pressurized vessel under conditions which maintain the
super-critical condition of the gas used for cleaning.
Normally, the cleaning is conducted at a temperature
range of about 35°C to about 100°C at about 1200 psi
25 (62,058 mmHg) to about 10,000 psi (517,149 mmHg) pressure
and preferably about 40°C to about 50°C and about 3,000
psi (155,145 mmHg) to about 8,000 psi (413,719 mmHg)
pressure. Inert gases having a critical temperature
below about 200°C are considered most advantageous in
30 the practice of the present invention. Examples of
such gases are alkanes and especially lower alkanes
such as ethane, propane and butane, alkenes and especially
lower alkenes such as ethylene, propylene and butylene,
dialkyl ethers such as dimethyl ether, SO₂, CO₂,



1 halogenated alkanes such as CHF_3 , CClF_3 , CFCI_3 , $\text{CF}_2=\text{CH}_2$,
2 CF_3 , $\text{CF}_3\text{-CF}_2\text{-CF}_3$, CF_4 , $\text{CH}_3\text{-CF}_3$, CHCl_2F , CCl_2F_2 , N_2O ,
3 noble gases such as argon, NH_3 and N_2 . Gases such as
4 CO_2 are preferred in the practice of the present
5 invention as the super-critical temperature of such
gases is near ambient temperature; the gases are
inexpensive, non-toxic, and relatively inert to most
solid substrates. CO_2 is especially preferred as this
gas in the super-critical state has a very low viscosity,
10 namely 0.05 centipoise, which is one-twentieth that of
water. As a result, the gas in the super-critical
state can penetrate very readily into the contaminant
to effect its rapid removal from the article being
cleaned.

15 To promote the rapid cleaning of the article
with the super-critical gas, it is further advantageous
to the practice of the present invention that the
article to be cleaned be preheated prior to its place-
ment in the pressure vessel to a temperature above
20 ambient, e.g., about 30°C to about 100°C , and preferably
about 40° to 50°C .

25 The absorptive capacity of the gases in the super-
critical condition with respect to most contaminants,
and particularly contaminants of basically organic
origin, is raised with increased pressure. Thus, when
practicing the cleaning procedure in accordance with
the practice of the present invention, a pressure which
is substantially higher than the critical pressure of
the gas and a temperature only slightly above the
30 critical temperature is selected for maintaining the
gas in the super-critical condition.



1 It is still further advantageous to the practice
of the present invention that the temperature and
pressure conditions under which the gas is caused to
contact the article to be cleaned be sufficiently
5 above the critical temperature and pressure in order
to have a single physical phase, i.e., the gaseous
phase, of the gas present in the pressurized vessel
during the cleaning operation. Thus, for CO₂ which
has a critical temperature of 32°C and a critical
10 pressure of 1073 psi (55,490 mmHg), when such gas is
used as the cleaning medium, the gas is maintained at a
temperature of about 35°C to about 100°C and a pressure
of 2,000 psi (103,430 mmHg) to 10,000 psi (517,149 mmHg)
15 in the pressure vessel.

15 In effecting cleaning of the surfaces of articles
in accordance with the practice of the present invention,
the article, when placed in the pressure vessel for
cleaning, is contacted with the gas under super-critical
conditions for a period of time ranging from about
20 0.25 hour to about four hours and preferably about 0.5
hour to about one hour to effect complete removal of
contaminants.

25 After sufficient time has elapsed in the pressure
vessel for the contaminants to be absorbed by the gas
and removed from the articles, the pressure in the
vessel is released and the gas containing the absorbed
contaminants are vented or purged from the vessel
into the atmosphere. When ambient pressure is attained,
the cleaned article is then removed from the vessel.



1 If it is intended that the gas be recycled for
reuse in removing contaminants, the gas in the super-
critical condition is vented or purged from the
pressurized vessel into a suitable collection vessel
5 where the pressure is reduced or the temperature lowered
at constant pressure, which conditions render the gas a
non-solvent for the contaminant which then precipitates
from the gas. The gas, freed of contaminants, can then
be recompressed and recycled for use in the cleaning
10 of contaminated articles.

15 The following are examples showing the cleaning
of various articles of manufacture using gases in the
super-critical condition according to the method of
the present invention.

15

Example I

20 A high pressure autoclave (10,000 psi or
517,149 mmHg maximum working pressure) of 300 milliliter
(ml) capacity was equipped with a gas inlet, a gas
outlet, pressure gauge, a thermocouple well, and heating
means. Connected to the gas inlet was a CO₂ supply
bottle which delivered the CO₂ at 800 psi (41,372 mmHg)
gauge. A gas booster pump operating on the 100 psi
(5171 mmHg) shop air and having the capability to raise
25 the bottle pressure to a maximum to 10,000 psi
(517,149 mmHg) was connected to the CO₂ bottle. The
autoclave was purged with CO₂ and heated to 100°F
(37.8°C). An O-ring formed of silicone rubber, weighing
0.460 grams, was placed in the autoclave. CO₂ gas was
30 fed to the booster pump and the autoclave was pressurized
to 8,000 psi (413,719 mmHg).

35



1 After contact of the O-ring with the CO₂ at
100°F (37.8°C) and 8,000 psi (413,719 mmHg) pressure
for one hour, the pressure in the autoclave was released
and the CO₂ containing the absorbed contaminants was
5 vented to the atmosphere. When ambient pressure was
attained in the autoclave, the cleaned O-ring was
removed from the autoclave and weighed to determine the
extractable weight loss effected by the cleaning
operation. The weight loss was determined to be 0.011
10 grams which represented the removal of 2.4 weight
percent (wt. %) contaminants.

By way of contrast, an identical silicone rubber
O-ring weighing 0.494 grams, was cleaned using an all
glass thermal vacuum cleaning unit wherein the O-ring
15 was heated for 120 hours and 180°C under a vacuum of
approximately 10⁻⁵ torr (mmHg). The extractable weight
loss was determined to be 0.0014 grams, representing
the removal of 0.4 wt. % contaminants. Subsequent
contact of the thermal vacuum cleaned O-ring with
20 isopropanol solvent at ambient laboratory temperature
removed another 0.004 grams of contaminant or an
additional 0.8 wt. % representing a total contaminant
removal of only 1.1 wt. %.

To determine the effect of the super-critical CO₂
25 treatment on the physical properties of the silicone
rubber material, O-rings which had been treated in
accordance with the procedure of Example I were subjected
to tensile and hardness tests used for the evaluation
of rubber mechanical and physical properties.

30 The results of these tests are recorded in
Table I below.

1

TABLE I

5

Silicone Rubber Treatment	Tensile Strength* (psi) (mmHg)	Elongation* (%)	Hardness* (Shore A)
<u>Super-critical</u>			
CO ₂	854 44,165	132	75
None	907 46,905	158	72

15
10
15
20
25
30
35
*Average of six tests

The results recorded in Table I show that the treatment of silicone rubber with CO₂ under super-critical conditions produces only a minor change in the mechanical and physical properties of the rubber.

Example II

The procedure of Example I was repeated to clean a polyimide polymer containing contamination in the form of volatile solvents by exposure to CO₂ for one hour under super-critical conditions of 8,000 psi (413,719 mmHg) pressure and a temperature of 45°C.

The amount of volatile contaminants remaining in the polymer after cleaning was determined by the American Society for Testing and Materials (ASTM) TEST E-595, described in the 1981 Annual Handbook of ASTM Standards,



1 under conditions of 125°C temperature and a vacuum of 10⁻⁵ torr (mmHg) or thermogravimetry mass spectrometry (TGA-MS) under conditions of one atmosphere and temperatures of 210°C or 820°C.

5 The results of these tests are recorded in Table II below.

10 For purposes of contrast, identical samples of the polyimide polymer were cleaned using thermal vacuum cleaning conditions wherein the polymer sample was heated for four hours at 80°C under a vacuum of approximately 10⁻⁵ torr (mmHg).

15 The results of these comparative tests are also recorded in Table II below.

15

TABLE IIVolatiles Remaining in Polyimide Polymer

20

Sample No.	Super-critical CO ₂ Cleaning	Thermal Vacuum Cleaning	Analysis Conditions
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25

1	0.56%	8.31%	ASTM E-595
2	0.76%	6.50%	ASTM E-595
3	1.00%	6.00%	TGA-MS, 210°C
4	37.00%	47.00%	TGA-MS, 820°C

30

The reduction in volatiles is important in polymer processing as it suppresses the formation of voids and areas of weakness in the finished product.

35



1 By reference to Table II, it is immediately apparent
that by the practice of the present invention the removal
of volatiles from polymeric products can be achieved to
a much greater degree in a shorter period of time as
5 compared to the practice of the prior art as represented
by thermal vacuum cleaning.

Example III

10 The procedure of Example I was repeated with the
exception that thin-sectioned parts of less than 0.25
inch thickness of a diverse selection of organic and
inorganic materials were cleaned by exposure to CO₂
under super-critical conditions with only minor changes
15 in the mechanical and physical properties of the
materials being observed thereafter.

The materials exposed to the super-critical CO₂
conditions were as follows:

- A. Laser casting alloy.
- B. Fluorosilicone sheet.
- C. Glass reinforced epoxy resin
multilayer sheet.
- D. Fiberized carbon.
- E. Absorptive fabric containing activated
carbon.
- F. Phenolic laminate cloth.
- G. Polyimide resin sheet.
- H. Quartz crystal assembly.
- I. Cryogenic cooler part.

30 The laser casting alloy was subjected to a vacuum-
pressure cycle in silicone oil (Dow-Corning DC-200) to
saturate the metal with the silicone oil. The oil-
saturated metal part was then cleaned according to
35 Military Interim Specification (MIS) 23542D, a cleaning
specification for these parts. According to MIS-23542D,



1 the material to be cleaned is subjected to an exhaustive
extraction in a Soxhlet apparatus using toluene as the
solvent followed by evaporation of the solvent and an
infrared (IR) spectra examination of the residue. In
5 accordance with MIS-23542D, the IR examination
must indicate the absence of silicone or other
residues to establish removal of all traces of silicone
oil contaminant. To achieve this result required four
10 days of treatment with the Soxhlet extraction apparatus,
whereas by using the procedure of Example I, removal
of all traces of silicon oil contaminants from a similar
laser casting alloy similarly saturated with silicone
oil was achieved in two hours.

While specific components of the present system
15 are defined above, many other variables may be introduced
which may affect, enhance or otherwise improve the
present invention. These are intended to be covered
herein. Further, while variations are given in the
present application, many modifications and ramifications
20 will occur to those skilled in the art upon reading the
present disclosure. These, too, are intended to be
included herein.



CLAIMSWhat is Claimed is:

- 1 1. A method of removing from a solid article contaminants adhering to the surfaces of the article, which comprises:
 - 1 placing the article having contaminants
 - 5 affixed to the surfaces thereof in a pressure vessel;
 - introducing a gas into the vessel and
 - maintaining the gas at a temperature and pressure at which the gas is placed in a super-critical condition;
 - maintaining the article in contact with the
 - 10 super-critical gas for a time sufficient to effect
 - absorption of the contaminants by the gas; and
 - removing the gas containing the contaminants from the vessel, whereby the contaminants are separated and removed from the article.
- 1 2. The method of Claim 1 wherein the gas is carbon dioxide.
- 1 3. The method of Claim 2 wherein the carbon dioxide is maintained in the vessel at a temperature in the range of about 35°C to about 100°C and a pressure of about 1,500 psi (77,572 mmHg) to about
- 5 10,000 psi (517,149 mmHg).
- 1 4. The method of Claim 1 wherein the contaminants are composed of organic-based materials.
- 1 5. The method of Claim 1 wherein the article is maintained in contact with the gas in the super-critical state for a period of time ranging from about 0.25 to about four hours.



1 6. The method of Claim 1 wherein the article
comprises a rubber.

1 7. The method of Claim 1 wherein the article
comprises a metal.

1 8. The method of Claim 1 wherein the article
comprises a synthetic organic polymer.

1 9. The method of Claim 1 wherein the article
comprises a polyimide polymer.

1 10. The method of Claim 1 wherein the article
comprises carbon.

1 11. The method of Claim 1 wherein the article
comprises a quartz crystal.

1 12. The method of Claim 1 wherein the article
comprises an assembly of parts.

1 13. The method of Claim 1 wherein the contaminant
is removed from the external surface of the article by
the gas.

1 14. The method of Claim 1 wherein the contaminant
is removed from the interstices of the article.



AMENDED CLAIMS

(received by the International Bureau on 25 April 1984 (25.04.84))

1 1. A method of removing from a solid structural component or element contaminants produced during the manufacture and processing of the component or element and adhering to the surfaces of the component or element,
5 which comprises:

 placing the component or element having contaminants affixed to the surfaces thereof in a pressure vessel;

10 introducing a gas into the vessel and maintaining the gas at a temperature and pressure at which the gas is placed in a super-critical condition;

 maintaining the component or element in contact with the super-critical gas for a time sufficient to effect absorption of the contaminants by the gas;
15 and

 removing the gas containing the contaminants from the vessel, whereby the contaminants are separated and removed from the component or element.

1 2. The method of Claim 1 wherein the gas is carbon dioxide.

1 3. The method of Claim 2 wherein the carbon dioxide is maintained in the vessel at a temperature in the range of about 35°C to about 100°C and a pressure of about 1,500 psi (77,572 mmHg) to about
5 10,000 psi (517,149 mmHg).

1 4. The method of Claim 1 wherein the contaminants are composed of organic-based materials.



1 5. The method of Claim 1 wherein the component or element is maintained in contact with the gas in the super-critical state for a period of time ranging from about 0.25 to about four hours.

1 6. The method of Claim 1 wherein the article comprises a rubber.

1 7. The method of Claim 1 wherein the article comprises a metal.

1 8. The method of Claim 1 wherein the article comprises a synthetic organic polymer.

1 9. The method of Claim 1 wherein the article comprises a polyimide polymer.

1 10. The method of Claim 1 wherein the article comprises carbon.

1 11. The method of Claim 1 wherein the article comprises a quartz crystal.

1 12. The method of Claim 1 wherein the article comprises an assembly of parts.

1 13. The method of Claim 1 wherein the contaminant is removed from the external surface of the component or element by the gas.

1 14. The method of Claim 1 wherein the contaminant is removed from the interstices of the component or element.



STATEMENT UNDER ARTICLE 19

The above-listed amendments are being submitted in accordance with the Patent Cooperation Treaty Article 19 and have been made for the following purposes.

Claim 1 has been amended to more particularly point out that the claimed process is used for the treatment of solid structural components or elements, as opposed to a particulate material, such as an adsorbent. In addition, Claim 1 has been amended to more particularly point out that the contaminants removed by the process of the present invention are contaminants produced during the manufacture and processing of the structural component or element, as opposed to an adsorbate which is intentionally adhered to an adsorbent as part of a purification process. These changes are deemed to clearly distinguish Applicant's claimed process over the references cited in the international search report.

Claims 5, 13, and 14 were each amended to provide language which is consistent with the language of Claim 1 from which these claims depend.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 83/01713

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC ³ : B 08 B 7/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
IPC ³	B 08 B; B 01 D
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵	

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 4124528 (MODELL) 7 November 1978 see the entire document cited in the application --	1-14
X	US, A, 3969196 (ZOSEL) 13 July 1976 see the entire document -----	1-14

* Special categories of cited documents: ¹⁶

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁹

13th February 1984

Date of Mailing of this International Search Report ²⁰

02 MARS 1984

International Searching Authority ²¹

EUROPEAN PATENT OFFICE

Signature of Authorized Officer ²²

G.L.M. Kruydenberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 83/01713 (SA 6067)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/02/84

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4124528	07/11/78	DE-A- 2544116 US-A- 4061566 GB-A- 1522352 JP-A- 51061484 CA-A- 1064891	08/04/76 06/12/77 23/08/78 28/05/76 23/10/79
US-A- 3969196	13/07/76	NL-A- 6404125 BE-A- 646641 DE-A, B, C 1493190 CH-A- 441232 GB-A- 1057911 FR-A- 1390751	19/10/64 16/10/64 18/09/69 15/01/68

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